

Thermodynamical identities—a systematic approach

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Abstract

We present a systematic approach to thermodynamical identities and illustrate the power of these methods by displaying Mathematica notebooks to deal with a large variety of such identities. In concrete examples these can involve rather tedious, not to say impossible, computations when done by hand.

1 Introduction

The subject of thermodynamics is notoriously difficult for mathematicians. V.I. Arnold [Ar] famously put it in a nutshell as follows:

Every mathematician knows that it is impossible to understand any elementary course in thermodynamics.

He continues by explaining that

the reason is that [the] thermodynamics is based on a rather complicated mathematical theory, on [the] contact geometry.

In [Co] we presented an axiomatic approach to Gibbsian thermodynamics which avoided these difficulties and developed a systematic approach to the classical identities of thermodynamics. In this short article we wish to present a theory-free version of the latter topic with a view to making it directly accessible to readers without the theoretical framework presented in [Co].

The four Maxwell relations in thermodynamics, which are equivalent to the Jacobian identity $\frac{\partial(T, S)}{\partial(p, V)} = 1$, are our starting point. Geometrically, they mean that the corresponding map from the (p, V) -plane into the (T, S) -plane is area-preserving.

2 The notation

In order to develop a systematic approach we prefer to employ a mathematically neutral notation rather than the standard notation of thermodynamics. We begin by recalling the latter for the reader's convenience.

Our starting point is the situation where we are given the temperature T and the entropy S as functions of the pressure p and the volume V .

We use the following dictionary to jump between the purely mathematical notation and the thermodynamical one: u corresponds to T , v to S , p to x and V to y . For example, the thermodynamical equations

$$T = pV, \quad S = \frac{1}{\gamma - 1} \ln(pV^\gamma)$$

of the ideal gas (we are omitting constants) corresponds to

$$u(x, y) = xy, \quad v(x, y) = \frac{1}{\gamma - 1} (\ln x + \gamma \ln y).$$

It is a consequence of the Maxwell relations that one can define four energy type functions and we will discuss this in more detail below.

3 Thermodynamical identities—the basic machinery

We suppose that u and v are given as functions f and g of x and y . Thus $u = f(x, y)$, $v = g(x, y)$. When $J = 1$, simple manipulations with differential forms proved the basic identities:

$$\begin{aligned} du &= f_1 dx + f_2 dy, & dv &= g_1 dx + g_2 dy \\ dx &= g_2 du - f_2 dv, & dy &= -g_1 du + f_1 dv \\ du &= \frac{f_2}{g_2} dv + \boxed{\frac{1}{g_2}} dx, & dy &= \boxed{\frac{1}{g_2}} dv - \frac{g_1}{g_2} dx \\ du &= \frac{f_2}{g_1} dv - \boxed{\frac{1}{g_1}} dy, & dx &= \boxed{\frac{1}{g_1}} dv - \frac{g_2}{g_1} dy \\ dv &= \frac{g_1}{f_1} du + \boxed{\frac{1}{f_1}} dy, & dx &= \boxed{\frac{1}{f_1}} du - \frac{f_2}{f_1} dy \\ dv &= \frac{g_2}{f_2} du - \boxed{\frac{1}{f_2}} dx, & dy &= \boxed{\frac{1}{f_2}} du - \frac{f_1}{f_2} dx \end{aligned}$$

where we have highlighted the expressions which correspond to the Maxwell relations.

In thermodynamic notation these are

$$\begin{aligned}
dT &= f_1 dp + f_2 dV, & dS &= g_1 dp + g_2 dV \\
dp &= g_2 dT - g_1 dS, & dV &= -g_1 dT + f_1 dV \\
dT &= \frac{f_2}{g_2} dS + \frac{1}{g_2} dp, & dV &= \frac{1}{g_2} dS - \frac{g_1}{g_2} dp \\
dT &= \frac{g_2}{f_2} dS - \frac{g_1}{f_2} dV, & dp &= \frac{g_1}{f_2} dS - \frac{g_2}{f_2} dV \\
dS &= \frac{g_1}{f_1} dT + \frac{1}{f_1} dV, & dp &= \frac{g_1}{f_1} dT - \frac{f_1}{f_1} dV \\
dS &= \frac{g_2}{f_2} dT - \frac{1}{f_2} dp, & dV &= \frac{f_1}{f_2} dT - \frac{g_2}{f_2} dp
\end{aligned}$$

where we are using the key: $u \leftrightarrow T$, $v \leftrightarrow S$, $x \leftrightarrow p$, $y \leftrightarrow V$ introduced above. In order to isolate the underlying patterns, we now use a numerical code. Thus

$$\begin{aligned}
u &\rightarrow 3 \leftarrow T \\
v &\rightarrow 4 \leftarrow S \\
x &\rightarrow 1 \leftarrow p \\
y &\rightarrow 2 \leftarrow V.
\end{aligned}$$

Partial derivatives will be denoted by triples in brackets. $(3, 1, 2)$, for example, denotes $\frac{\partial u}{\partial x}|_y$ in the neutral notation, $\frac{\partial T}{\partial p}|_V$ in the thermodynamical one. In general, (i, j, k) denotes the derivative of the variable i , regarded as a function of the j -th and k -th variable, with respect to the j -th variable.

By reading off from the above list, we can express each partial derivative of the form (i, j, k) in terms of f_1, f_2, g_1, g_2 . For example:

$$(3, 1, 2) = f_1, \quad (3, 2, 1) = f_2, \quad (4, 1, 2) = g_1, \quad (4, 2, 1) = g_2;$$

$$(1, 3, 4) = g_2, \quad (2, 3, 4) = -g_1, \quad (1, 4, 3) = -f_2, \quad (2, 4, 3) = f_1;$$

and so on. We can then express any derivative (a, b, c) in terms of ones of the form $(d, 1, 2)$ or $(e, 2, 1)$. Thus the four derivatives with x and v as independent variables can be computed::

$$\begin{aligned}
(3, 4, 1) &= \frac{(3, 2, 1)}{(4, 2, 1)} \\
(2, 4, 1) &= \frac{1}{(4, 2, 1)} \\
(3, 1, 4) &= \frac{(4, 2, 1)}{(4, 1, 2)} \\
(2, 1, 4) &= -\frac{(4, 1, 2)}{(4, 2, 1)}
\end{aligned}$$

Then, as is standard in thermodynamics, we can introduce four energy functions E^{13} , E^{14} , E^{23} , E^{24} such that $dE^{24} = u dv - x dy$, $dE^{14} = u dv + y dx$, $dE^{13} = -v du + y dx$, $dE^{23} = -v du - x dy$ (the superfixes correspond to the independent variables—thus for E^{13} these are x and u i.e. 1 and 3).

We will discuss these in more detail below where the rationale of our notation will be explained. In terms of the classical notation:

$$\begin{aligned}
dE &= T dS - p dV \quad (\text{energy}) \\
dF &= -S dT - p dV \quad (\text{free energy}) \\
dG &= -S dT + V dp \quad (\text{Gibbs' potential}) \\
dH &= T dS + V dp \quad (\text{enthalpy}),
\end{aligned}$$

i.e., $E^{13} = G$, $E^{23} = F$, $E^{14} = H$ and $E^{24} = E$.

If we arrange the energy functions in lexicographic order i.e. as E^{13} , E^{14} , E^{23} , E^{24} and denote them by 5, 6, 7 and 8 in this order, then we can incorporate them into our system. For it follows from the definitions and simple substitutions that

$$\begin{aligned}
dE^{13} &= (y - v f_1) dx - f_2 v dy \\
dE^{14} &= (u f_1 + y) dx + u f_2 dy \\
dE^{23} &= -v f_1 dx + (x - v f_2) dy \\
dE^{24} &= u f_1 dx + (u f_2 - x) dy
\end{aligned}$$

and so

$$\begin{aligned}
(5, 1, 2) &= y - g f_1, & (5, 2, 1) &= -g f_2 \\
(6, 1, 2) &= y + f g_1, & (6, 2, 1) &= f g_2 \\
(7, 1, 2) &= -g f_1, & (7, 2, 1) &= -x - g f_2 \\
(8, 1, 2) &= f g_1, & (8, 2, 1) &= -x + f g_2.
\end{aligned}$$

One of the potentially irritating features of the thermodynamical identities is that many are related by a simple swapping of the variables while this is accompanied by changes of sign which seem at first sight to be random. The simplest example is displayed by the four Maxwell relations. We can

systematise such computations by introducing the symbol $[a, b; c, d]$ for the Jacobi determinant of the mapping $(c, d) \mapsto (a, b)$ i.e.

$$[a, b; c, d] = (a, c, d)(b, d, c) - (a, d, c)(b, c, d).$$

The determinant then takes care of the sign.

For example $[3, 4; 1, 2]$ is the Jacobian $\frac{\partial(u, v)}{\partial(x, y)}$ and so is 1 (in this case this denotes the number 1), $[3, 2; 4, 1]$ is $\frac{\partial(u, y)}{\partial(v, x)}$ and so is $-\frac{f_1}{g_2} = -\frac{(3, 1, 2)}{(4, 2, 1)}$. Note that there are 1,680 such Jacobians. However, lest the reader despair, we will display below simple rules which allow us to express them all in terms of our primitive quantities (f and g together with their partials and, of course, x and y). Later, we append a Mathematica notebook which computes all such expressions at the press of a button.

4 Higher derivatives

Some of the thermodynamical identities involve higher derivatives and we indicate briefly how to incorporate these into our scheme. We use the self-explanatory notation $((a, b, c), d, e)$ for second derivatives. Thus $((3, 1, 2), 2, 1)$ is just f_{12} . Note that this notation allows for such derivatives as $\left(\frac{\partial}{\partial T} \left(\frac{\partial E}{\partial p}\right)_V\right)_S$ which is $((8, 1, 2), 3, 4)$. Once again, we can express all such derivatives (there are now 18,816 of them) in terms of x, y, f, g and their partials (now up to the second order) using the chain rule. For

$$((a, b, c), i, j) = ((a, b, c), 1, 2)(1, i, j) + ((a, b, c), 2, 1)(2, i, j)$$

and (a, b, c) resp. $(1, i, j)$ and $(2, i, j)$ can be dealt with using the above tables.

We display below a Mathematica notebook which computes all expressions of the form $((a, b, c), d, e)$.

5 Derived quantities and thermodynamical identities

The reason why there is a plethora of thermodynamical identities is simple. A large number of significant (and also insignificant) quantities can be expressed or defined as simple algebraic combinations of a very few (our primitive quantities x, y, f, g and their partials). Hence there are bound to be many

relationships between them. Our strategy to verify (or falsify) an identity is to use the above methods to express both sides in terms of these quantities and check whether they agree.

Of course, there are myriads of such quantities and identities and we can only bring a sample. Thus we have

$$c_V = T \left(\frac{\partial S}{\partial T} \right)_V$$

the heat capacity at constant volume and

$$c_p = T \left(\frac{\partial S}{\partial T} \right)_p$$

the heat capacity at constant pressure. In our formalism, $c_V = f(4, 3, 2)$ and $c_p = f(4, 3, 1)$ and so, from our tables,

$$c_V = f \frac{g_1}{f_1}, \quad c_p = f \frac{g_2}{f_2}.$$

Hence for the important quantities $\gamma = \frac{c_p}{c_V}$ and $c_p - c_V$ we have $\gamma = \frac{f_2 g_1}{f_1 g_2}$ and $c_p - c_V = f \frac{1}{f_1 f_2}$.

We illustrate our method by verifying the simple identity:

$$c_p - c_V = T \left(\frac{\partial P}{\partial T} \right)_V \left(\frac{\partial V}{\partial T} \right)_p.$$

Using the tables above, we can easily compute both sides in terms of our primitive expressions and get $\frac{f}{f_1 f_2}$ in each case.

6 Computing (a, b, c) and $((a, b, c), d, e)$

We can summarise these results in the following formulae:

$$[a, b; c, d] = \frac{(a, 1, 2)(b, 2, 1) - (a, 2, 1)(b, 1, 2)}{(c, 1, 2)(d, 2, 1) - (c, 2, 1)(d, 1, 2)}$$

and so

$$(a, b, c) = [a, c; b, c] = \frac{(a, 1, 2)(c, 2, 1) - (a, 2, 1)(c, 1, 2)}{(b, 1, 2)(c, 2, 1) - (b, 2, 1)(c, 1, 2)}$$

which allow us to systematically compute any of the derivatives of the form (a, b, c) in terms of our primitives $x, y, f, g, f_1, f_2, g_1$ and g_2 .

For the second derivatives we substitute

$$\phi = \frac{(a, 1, 2)(c, 2, 1) - (a, 2, 1)(c, 1, 2)}{(b, 1, 2)(c, 2, 1) - (b, 2, 1)(c, 1, 2)}$$

into the formula

$$(\phi, d, e) = \frac{(\phi, 1, 2)(d, 2, 1) - (\phi, 2, 1)(d, 1, 2)}{(d, 1, 2)(e, 2, 1) - (d, 2, 1)(e, 1, 2)}$$

to compute $((a, b, c), d, e)$ in terms of our primitive terms (this time with the first and second derivatives of f and g). The advantage of these formulae is, of course, that one can write a simple programme to compute them. (It is always tacitly assumed in the above formula that the appropriate conditions which allows a use of the inverse function theorem hold).

The formulae developed here suffice to create Mathematica notebooks to calculate any of the above quantities both for the general case and for specific gas models and we display these below.

7 A notational survival kit

We emphasise that the numerical code for the various thermodynamical quantities is a mere construct to facilitate their computation (ideally with the aid of suitable software) and the final goal is to express them all in terms of the basic quantities $(x, y, f, g$ and the partials of the latter). It is then a routine matter to translate these into the standard terminology of thermodynamics if so required. For the convenience of the reader we give a dictionary of the relationships between them:

1	2	3	4	5	6	7	8
p	V	T	S	Φ	W	F	E
x	y	u	v	E^{13}	E^{14}	E^{23}	E^{24} .

Of course, p is pressure, V volume, T temperature, S entropy and Φ , W , F and E are free enthalpy, enthalpy, free energy and energy respectively.

8 Mathematica notebooks

8.1 A notebook for (a, b, c) , $[a, b; c, d]$ and $((a, b, c), d, e)$

We start with a notebook which computes (a, b, c) , $[a, b; c, d]$ and $((a, b, c), d, e)$ for any combination of a, b and c between 1 and 8.

```
Clear[ff1, ff2, ff3, ff4, ff5, ff, gg];
ff1[a_, 1, 2] =
  If[a == 1, 1,
    If[a == 2, 0,
      If[a == 3, D[ff[x, y], x],
        If[a == 4, D[gg[x, y], x],
          If[a == 5, y - gg[x, y] D[ff[x, y], x],
            If[a == 6, y + D[gg[x, y], x] ff[x, y],
              If[a == 7, -gg[x, y] D[ff[x, y], x],
                If[a == 8, D[gg[x, y], x] ff[x, y]]]]]]]]];

ff2[a_, 2, 1] =
  If[a == 1, 0,
    If[a == 2, 1,
      If[a == 3, D[ff[x, y], y],
        If[a == 4, D[gg[x, y], y],
          If[a == 5, -gg[x, y] D[ff[x, y], y],
            If[a == 6, D[gg[x, y], y] ff[x, y],
              If[a == 7, -x - gg[x, y] D[ff[x, y], y],
                If[a == 8, -x + ff[x, y] D[gg[x, y], y]]]]]]]]];

ff4[a_, b_, c_,
  d_] = (ff1[a, 1, 2] ff2[b, 2, 1] -
  ff2[a, 2, 1] ff1[b, 1, 2])/(ff1[c, 1, 2] ff2[d, 2, 1] -
  ff2[c, 2, 1] ff1[d, 1, 2]);
ff3[a_, b_, c_] = ff4[a, c, b, c];
ff5[a_, b_, c_, d_,
  e_] = (D[ff3[a, b, c], x] ff2[d, 2, 1] -
  D[ff3[a, b, c], y] ff1[d, 1, 2])/(ff1[d, 1, 2] ff2[e, 2, 1] -
  ff2[d, 2, 1] ff1[d, 1, 2]);
```

Here we have defined three functions ff3, ff4 and ff5 of 3, 4 and 5 arguments, the variables having whole number values between 1 and 8. The

inputs a, b, c , a, b, c, d or a, b, c, d, e yield the values (a, b, c) , $[a, b; c, d]$ and $((a, b, c), d, e)$ respectively. In order to show that it can cope with the most complicated gas models we have used the following one which combines the Van der Waals gas and the Feynman gas (see [Co] for details).

8.2 A synthesis

A number of models of real gases can be subsumed in the following one.

$$u = \phi \left(\left(x + \frac{a}{y^2} \right) (y - b) \right) \quad v = \ln \left(\left(x + \frac{a}{y^2} \right) (v - b)^{u(x,y)} \right).$$

γ , the adiabatic exponent, is a function of one variable and ϕ is a primitive of $\frac{1}{\gamma - 1}$. This model has the double advantage that it incorporates the van der Waals gas and also one introduced by Feynman which allows for the fact that in real gases, γ depends on temperature. If the constants a and b vanish, we get what we call the Feynman gas (this model appears in [Fe]—see [Co] for a more detailed description). We get the van der Waals gas when γ is constant and this specialises to the ideal gas when a and b vanish.

We can now compute any of the above expressions for this model, using the above notebook.

8.3 Thermodynamics identities and Gröbner bases

We can proceed further along the path to automatisation by invoking the concept and methods of Gröbner bases. Rather than give a systematic treatment, we again display a corresponding notebook.

The input below consists of two list of symbols which use an obvious code— $x412$, for example, denotes the partial derivative $(4, 1, 2)$. The second list is of the quantities which occur in the formulae we are interested in. They are regarded as variables and our setting is the ring of polynomials in these variables. This list can be chosen at the discretion of the user (there are too many candidates to include all of them in one notebook). The first list is of the relationships between these symbols (each expression is to be thought of as being set equal to zero) beginning with the Maxwell relation followed by the formulae deduced above. In order to keep things simple, we have only used the relationships which we computed above. They can, of course, be enriched by triples which were computed by the above Mathematica programme.

```
Clear[p, q]; p = {x312 x421 - x321 x412 - 1, x134 - x421, x143 + x321,
```

```

    x234 + x412, x243 - x312, x421 x341 - x321, x314 x421 - 1,
    x241 x421 - 1, x214 x421 + x412, x342 x412 - x312, x324 x412 + 1,
    x412 x142 - 1, x124 x412 + x421, x432 x312 - x412, x423 x312 - 1,
    x132 x312 - 1, x123 x312 + x321, x431 x321 - x421, x413 x321 + 1,
    x231 x321 - 1, x213 x321 + x312, x612 - x2 - x3 x412,
    x621 - x3 x421, x512 - x2 + x4 x312, x521 + x4 x321,
    x712 + x4 x312, x721 + x1 + x4 x321, x812 - x3 x412,
    x821 + x1 - x3 x421};
q = {x1, x2, x3, x4, x112, x121, x212, x221, x312, x321, x412, x421,
    x134, x143, x234, x243, x341, x314, x241, x214, x342, x324, x142,
    x124, x432, x423, x132, x123, x431, x413, x231, x123, x512, x521,
    x612, x621, x712, x721, x812, x821};
GroebnerBasis[p, q]

```

The output below is a (Gröbner) basis for the ideal generated by the above list of relationships in our polynomial ring. Hence every entry is, when set equal to zero, a (new) identity.

```

{x213 x621 + x712 + x213 x721 - x213 x821, x521 - x621 - x721 + x821,
x512 - x612 - x712 + x812,
x231 + x413, -x231^2 x621 + x431 x712 + x213 x431 x721 - x431 x812 -
x213 x431 x821, -1 + x123 x213, x621 + x123 x712 + x721 - x821,
x123 x231^2 x621 + x431 x621 + x123 x431 x812, x132 + x123 x231,
x123 x231 + x423, -x123 x231^2 - x431 + x432, x621 + x124 x812,
x124 x231^2 - x431 + x124 x213 x431,
x123 x124 x231^2 - x123 x431 + x124 x431, 1 - x124 x213 + x142 x231,
x124 x231 + x142 x431, x142 + x324,
x342 x712 + x213 x342 x721 + x142^2 x213 x812 - x342 x812 -
x213 x342 x821, x142 x213 + x231 x342, -x124 x213 + x342 x431,
x342 x621 - x142^2 x812 + x123 x342 x812,
x142^2 - x123 x342 + x124 x342,
x214 x712 + x213 x214 x721 - x213 x812 - x213 x214 x821,
x214 x621 + x812, -x231^2 - x213 x431 + x214 x431, -1 +
x124 x214, -x142^2 x213 x214 - x213 x342 + x214 x342,
x142 x214 + x241, x142 x214 + x314, -x142^2 x214 + x341 - x342,
x243 x712 + x213 x243 x721 + x142 x213 x812 - x243 x812 -
x213 x243 x821, x213 + x231 x243,
x243 x621 - x142 x812 + x123 x243 x812, x142 - x123 x243 + x124 x243,
x142 x243 - x342, -x142 x213 x214 - x213 x243 + x214 x243, -x231 +
x234 + x243 x431, x143 - x123 x243, x134 + x123 x243 x431,

```

$$\begin{aligned} & x_{421} + x_{123} x_{243} x_{431}, x_{231} + x_{412} - x_{243} x_{431}, \\ & x_{123} x_{243} + x_{321}, -x_{243} + x_{312}, \\ & x_4 + x_{231} x_{621} + x_{231} x_{721} - x_{231} x_{821}, x_3 - x_{142} x_{812}, \\ & x_2 - x_{612} + x_{812}, x_1 - x_{621} + x_{821} \} \end{aligned}$$

The literature: The method of Gröbner bases which is used in Mathematica is based on the so-called Buchberger algorithm (see [Bu]) and there is an extensive literature about it.

We would also like to mention two works ([Br] and [Ja]) which are dedicated to the development of systematic approaches to thermodynamical identities and which were useful in our approach.

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